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Ion-Exchange Resin for Removing Hexavalent Chromium from Ground Water at Treatment Facility C: Data on Removal Capacity, Regeneration Efficiency, and Operation

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Introduction

Lawrence Livermore National Laboratory (LLNL) is operated for the Department of Energy by the University of California. In July 1987, the LLNL Livermore site was placed on the National Priorities List based on the presence of volatile organic compounds (VOCs) in ground water. The July 1992 Record of Decision (ROD) stipulates air stripping for treatment of VOCs and ion-exchange to treat chromium in the ground water for Treatment Facility C (TFC). TFC was activated in October 1993.

TFC is designed to treat influent ground water at 60 gpm with concentrations of total VOCs at an average of 130 ppb, and hexavalent chromium at an average 30 ppb.1 LLNL discharges the ground water to a surface arroyo under the Waste Discharge Requirement Order No. 91-091. Under this agreement, the effluent limitation for total VOCs is 5 ppb, and for hexavalent chrome is 11 ppb. Air stripping removes the VOCs to below the limit of detection in ground water (0.5 ppb). The ion exchange system removes the hexavalent chromium to below its limit of detection (2 ppb).

TFC was constructed inside a permanent building. Submersible pumps extract the ground water from well fields located near the building. Inside the facility, the ground water is filtered to remove particulate and sediment to a nominal 5 microns, then passed through two tank-type air strippers in series, where the VOCs are removed and collected onto vapor-phase granular activated carbon. The ground water then travels through two columns, connected in series, that are filled with ion exchange resin. After passing through both ion exchange columns, the treated ground water is discharged to a nearby ditch.

The two ion exchange columns contain 30 ft3 of resin each. They are part of a larger system called the hexavalent chromium removal unit (HCRU). The HCRU has an internal programmable logic controller (PLC). Process hardware consists of a batch tank, pump, sand filter, ion exchange columns, and valving and piping for treated water. The HCRU also contains a salt tank, pump, and separate piping for regenerating the resin. Regeneration is done counterflow to the process flow direction. Both normal water processing and the regeneration sequence are automatically sequenced by the PLC. During normal processing, the effluent ground water is sampled in between the columns for hexavalent chrome. When the level between the two columns exceeds 11 ppb, the upstream column is regenerated and placed back in service as the downstream column. In this way the freshly regenerated resin serves as the back-up column.

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[1]Lawrence Livermore National Laboratory, *Draft Remedial Design Report No. 2 for Treatment Facilities C and F*, (UCRL-AR-112814 dr), May 10, 1993.

Chromium removal from the ground water

The resin used is a strongly basic Type I quaternary ammonium anion exchange resin with a styrene-divinylbenzene copolymer gel matrix. It has a nominal capacity of 1.5 eq/L of resin bed. The study using this particular resin covered two years of operation, and the total hexavalent chromium removed from the ground water as of June 8, 1995 was 667 grams. This resin is used in the chloride form, where chloride is the mobile ion which is "exchanged" for a mobile counterion in the ground water.

The influent chromium level is 0.035 mg Cr(VI)/L present as the CrO_4^{2-} anion. Other anions and cations present in the TFC influent ground water at the milligram/liter level are bicarbonate (290 mg/L as $CaCO_3$), chloride (100), nitrate (24), sulfate (34), magnesium (21), calcium (60), and sodium (130). The pH is 7.3, and TDS is 560 mg/L.

This resin was tested at LLNL using ground water similar to that at TFC in a bench-top test before selection for the field.[2] The bed volumes (BV) of water treated before effluent chrome levels exceeded 11 ppb were 4860. The results were not as promising as the results from Clifford's study using a Scottsdale, Arizona well, in which 20,700 BV were treated before effluent chrome levels exceeded 10 ppb[3]. It is suggested in Reference 2, that at low levels of Cr concentration, the bed volumes scale linearly with sulfate concentration. The sulfate concentration in Clifford's study was one-fifth the sulfate concentration in the bench-top test.

The multicomponent ion exchange effects are made evident by pH swings in brand-new resins and in a resin column freshly regenerated. Initially the pH swings low (4.8) as the bicarbonate ions are removed from the water. Since bicarbonate ion is less preferred than the presaturant ion, it will have a gradual breakthrough, and the pH will gradually approach influent pH levels (7.3). If chromatographic peaking were to occur, where the least preferred species is concentrated in the column and at some time exits the column in concentrations exceeding the influent concentrations, the pH could also increase above 7.3. We have observed such pH behavior at TFC. For two columns with new, unused Type II strongly basic gel anion exchange resin, nearly 36,000 gallons (80 BV) of ground water were passed through the columns before the effluent rose to above our lower discharge limit of 6.5.

Hexavalent chrome removal capacity at TFC

The amount of water treated by the resin at TFC when it was first put on-line was 7,173 BV before exceeding 11 ppb at the effluent. This translates to an operating capacity of 7 g CrO_4^{2-} removal per ft^3 of resin. At this point the column was regenerated and put back in line in the downstream position. The amount of water treated before the effluent of the first column again exceeded 11 ppb was 6,646 BV. A steady decrease of number of bed volumes of water treated was observed over the next two years.

Rate of breakthrough

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[2]Richard A. Torres, *Removing Hexavalent Chromium from Subsurface Waters with Anion-Exchange Resin*, (UCRL-ID-114369, National Technical Information Service, June 1995).

[3]Dennis A. Clifford, (1990) in *Water Quality and Treatment*, Chapter 9, Ed. 4, Pontius, F. Ed., McGraw Hill, New York.

The first time the columns experienced breakthrough of chromium, the number of bed volumes for the effluent to increase from 3 to 11 ppb was 1500 BV. Later regenerations differed, having volumes of 860 and 2000 BV. More study needs to be done to understand this variation in rate of breakthrough. Both the expected capacity and expected breakthrough bed volumes are important to know in planning for monitor sampling of the HCRU.

Regeneration

The regeneration process was optimized to minimize waste produced and maximize regeneration of the resin. The HCRU regenerates the columns counter flow to the process flow. In our bench top tests, it was determined that NaOH was not necessary to achieve good regeneration, thus regeneration at TFC is done with NaCl alone. After an initial backwash to fluff the bed, a 3.2 molar NaCl solution is injected at 0.2 gpm/ft^3. Approximately 450 gallons of brine is used to regenerate one 30 ft^3 resin column. The total rinse volume is about 470 gallons or about 2 bed volumes. The initial rinse along with the regenerate solution is disposed of as waste. To insure the rinse amount was adequate, the residual NaCl in the rinse water was measured with a chloride meter. After approximately 380 gallons, the residual NaCl concentration in the rinse water was below 1%.

We have calculated the regeneration efficiency as the ratio of the chrome eluted off the columns to the total chrome loaded onto the columns. We have seen a regeneration efficiency of approximately 50% for the facility overall since it was brought on line. The regeneration efficiency at the first regeneration of column B was 18%. Later, the cumulative regeneration efficiency for column B increased to 47%. The concentration of the NaCl and the amount of salt solution injected through the column were increased until the regeneration efficiency was optimized for the existing HCRU.

Other anions removed by the resin

In the regeneration solution analysis, along with the chromate, we have seen increased concentrations of chloride, sulfate, and nitrate, as compared to their concentrations in the influent ground water, with chromium having the largest increase. There was no arsenic in the regeneration solutions that we tested. We have also seen levels of $potassium_{40}$ and uranium. We believe the potassium and uranium to be naturally-occurring in our ground water. The presence of both of these contaminates resulted in the regeneration waste having to be disposed of as mixed waste. When the resin was removed it was also treated as mixed waste.

Cost

The HCRU was contracted to an external supplier. The HCRU, including the initial resin, cost $156 K. The estimated yearly cost to operate the HCRU are as follows: Salt, $1K; resin replacement, $6K; filter, valve, pump maintenance, $2K.

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